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54 Polyester composition.

57 A polyester composition comprising:

(A) 100 parts by weight of substantially linear polyester comprising, as the main constituent unit, ethylene terephthalate;

(B) 0.05 to 15 parts by weight of crystallization promotor; and

(C) 0.1 to 15 parts by weight of at least one modified polyolefin wax plasticizer selected from oxidized polyolefin waxes, unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes, unsaturated epoxy compound-modified polyolefin waxes, unsaturated silane compound-modified polyolefin waxes, and styrene-type monomer-modified olefin waxes.

EP 0 255 735 A2

POLYESTER COMPOSITION

The present invention relates to a polyester composition comprising, as the main constituent unit, ethylene terephthalate and having excellent heat resistance and an improved rate of crystallization.

Substantially linear polyesters comprising, as the main constituent unit, an ethylene terephthalate, such as polyethylene terephthalate, have been heretofore used as a material for molded articles having various shapes, such as a film, a sheet, a laminate, and a container, because of their excellent stiffness, heat resistance, and gas barrier properties. However, these polyesters are disadvantageous in that the rate of crystallization is slow and they cannot be molded at a high speed. Therefore, a means of elevating the temperature of the mold is used to enhance the rate of crystallization of the polyesters. However, use of this means involves disadvantages in that the resin undergoes thermal deterioration and the molded article tends to be warped.

In order to increase the rate of crystallization and to improve the mechanical properties such as heat resistance and stiffness, of the polyesters, there have been proposed methods comprising blending various additives with the polyesters. These methods include the blending of inorganic compounds such as talc, metal salts of aliphatic or aromatic carboxylic acids, or polymers such as polyalkylene glycols, alkoxy polyalkylene glycols, ethylene-(meth)acrylic acid salt copolymers, unsaturated polyester, and polyamides with the polyesters. For example, United States Patent 3,639,527 proposes copolymers of ethylene or styrene with salts of acrylic and methacrylic acid or the like. United States Patent 4,352,904 and U.K. Patent application GB 2,015,013 propose techniques of blending (1) fillers or the like, (2) sodium or potassium salts of organic polymers having pendant carboxyl groups, and (3) organic esters. Examples of the salts of organic polymers (2) are sodium salts of ethylene-methacrylic acid copolymers and sodium salts of styrene-maleic anhydride copolymers. Japanese Unexamined Patent Publication Nos. 56-145943, 56-127655, and 57-145145 propose techniques of blending the same copolymer salts as those described in (2) above and polyalkylene glycols or their derivatives.

Japanese Unexamined Patent Publication Nos. 56-109244 and 56-109245 propose a technique of blending polyethylene wax, optionally a nucleating agent and a crystallization promoter with a polyethylene terephthalate resin. Similarly, United States Patent 3,405,198 discloses the technique of blending polyethylene.

Japanese Unexamined Patent Publication No. S 58-76446 and 57-8241 propose techniques of blending specific polyethers or polyesters. UK Patent Specification GB 1282679 and Japanese Unexamined Patent Publications Nos. 51-148744, 57-38847 and 58-63743 propose a technique of blending metal salts of carboxylic acids.

The present invention provides a polyester composition comprising :

(A) 100 parts by weight of substantially linear polyester comprising, as the main constituent unit, ethylene terephthalate;

(B) 0.05 to 15 parts by weight of crystallization promoter; and

(C) 0.1 to 15 parts by weight of at least one plasticizer selected from (C<sub>1</sub>), (C<sub>2</sub>), (C<sub>3</sub>), and (C<sub>4</sub>) which are defined as follows:

(C<sub>1</sub>) condensation product of compound of the formula (I):

$(HQ - R)_2S(I)$

(wherein the R groups are the same or different and selected from aliphatic, alicyclic, and aromatic hydrocarbon groups and any combination thereof, and the Q groups are the same or different and selected from oxygen and sulfur) with organic compound containing two groups selected from alcoholic and phenolic hydroxyl groups;

(C<sub>2</sub>) ester compound derived from organic acid and compound selected from compounds of the above-mentioned formula (I) and condensation products (C<sub>1</sub>);

(C<sub>3</sub>) ether compound derived from (i) compound selected from compounds of the above-mentioned formula (I) and condensation products (C<sub>1</sub>), and (ii) compound selected from monohydric alcohols and monohydric phenols; and

(C<sub>4</sub>) modified polyolefin wax selected from oxidized polyolefin waxes, unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes, unsaturated epoxy compound-modified polyolefin waxes, unsaturated silane compound-modified polyolefin waxes, and styrene-type monomer-modified olefin waxes.

**Component (A)**

The polyester (A) incorporated into the polyester composition of the present invention is a substantially linear polyester comprising, as the main constituent unit, ethylene terephthalate. It may contain at least 70 mole %, preferably at least 80 mole %, more preferably at least 85 mole % of the ethylene terephthalate constituent unit.

The dicarboxylic acid component units of the polyester may contain a small amount of aromatic dicarboxylic acid component units other than terephthalic acid component units. The aromatic dicarboxylic acid component units other than the terephthalic acid component units may include, for example, isophthalic acid, phthalic acid, and naphthalene dicarboxylic acid.

The diol component units of the polyester may contain a small amount of diol component units other than ethylene glycol component units. The diol component units other than ethylene glycol component units may include, for example, diol component units having 3 to 20 carbon atoms such as propylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,4-bis( $\beta$ -hydroxyethoxy) benzene, 1,3-bis( $\beta$ -hydroxyethoxy) benzene, 2,2-bis(4- $\beta$ -hydroxyethoxyphenyl) propane, bis (4- $\beta$ -hydroxyethoxyphenyl)sulfone, bis (4-hydroxyphenyl)methane, and 2,2-bis(4-hydroxyphenyl)propane, and polyalkylene glycol units having a molecular weight of 300 to 10,000 such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol.

The polyester of the present invention may optionally contain a small amount of polyfunctional compounds, in addition to the above-mentioned aromatic dicarboxylic acid component units and the above-mentioned aromatic dicarboxylic acid component units and the above-mentioned diol component units. Examples of such polyfunctional compound component units are aromatic polybasic acids such as trimellitic acid, trimesic acid, pyromellitic acid, and 3,3',5,5'-tetra-carboxydiphenyl; aliphatic polybasic acids such as butanetetracarboxylic acid; aromatic polyols such as phloroglucin and 1,2,4,5-tetrahydroxybenzene; aliphatic polyols such as glycerol, trimethylethane, trimethylolpropane and pentaerythritol; and oxypolycarboxylic acids such as tartaric acid and malic acid.

Furthermore, the polyester of the present invention may contain a small amount of hydroxycarboxylic compounds such as p-hydroxybenzoic acid as a constituent unit, in addition to the above-mentioned aromatic dicarboxylic acid component units, diol component units, and polyfunctional compounds.

The polyester composition is such that the content of the terephthalic acid component unit is usually in the range of from 40 to 51 mole %, preferably from 43 to 50.5 mole %; the content of the aromatic dicarboxylic acid component unit other than the terephthalic acid component unit is usually in the range of from 0 to 10 mole %, preferably from 0 to 7 mole %, the content of the ethylene glycol component unit is usually in the range of from 35 to 51 mole %, preferably from 40 to 50.5 mole %; the content of the diol component unit other than the ethylene glycol component unit is usually in the range of from 0 to 15 mole %, preferably from 0 to 10 mole %, and the content of the polyfunctional compound unit is usually in the range of from 0 to 10 mole %, preferably from 0 to 8 mole %. The polyester of the present invention usually has an intrinsic viscosity  $[\eta]$  of 0.45 to 2.0 dl/g, preferably 0.50 to 1.8 dl/g, determined in p-chlorophenol at a temperature of 50°C. The polyester usually has a melting point of 180°C to 280°C, preferably 200°C to 270°C, and a glass transition temperature of 40°C to 140°C, preferably 50°C to 120°C.

With respect to the expressions "constituent unit" or "component unit", it should be noted that the acids and alcohols described above are not always used as the direct starting materials in production of the polyester of the invention.

**Component (B)**

The crystallization promoters (B) incorporated into the polyester composition of the present invention may be any known crystallization promoters. Examples of such crystallization promoters are solid inorganic compounds such as talc and clay; salts of organic carboxylic acids such as caproic acid, stearic acid, montanic acid, benzoic acid and terephthalic acid, e.g., sodium and potassium salts of these carboxylic acids.

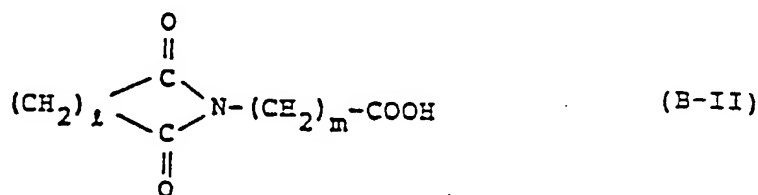
The inventors found that an alkali metal salt or alkaline earth metal salt of a specific organic carboxylic acid containing an imido linkage and having not greater than 50 carbon atoms, preferably 6 to 45 carbon atoms, more preferably 6 to 40 carbon atoms, in an excellent crystallization promoter.

Such carboxylic acids are usually those having the formula (B-I)

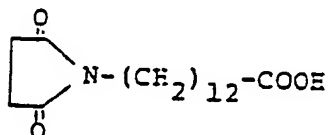
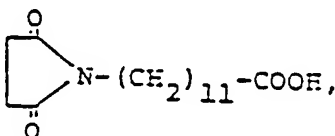
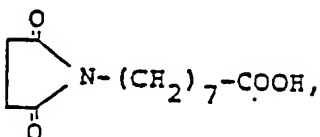
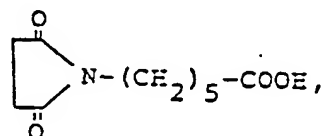
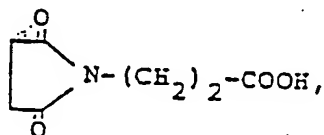


wherein,  $\text{X}^1$  and  $\text{X}^2$  (these are collectively referred to as X, hereinafter, may be combined with each other and are preferably in the combined form), and Y each represents an aliphatic group, an alicyclic group, an aromatic group or a combination thereof, and at least one of X and Y contains a carboxyl group, and further, X and Y may contain a member selected from the group consisting of a halogen atom, a nitro group and an amino group, and when X contains a carboxyl group; Y may be a hydrogen.

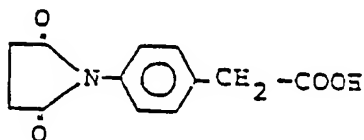
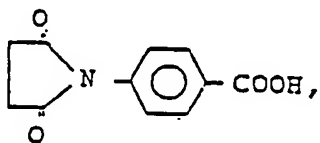
Among the carboxylic acids of the formula (B-I), the preferred carboxylic acids are those in which X represents an aliphatic group are those having the formula (B-II):



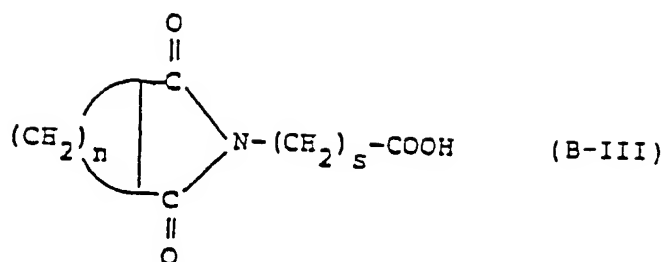
wherein  $l$  is 2 to 3, and  $m$  is an integer of 1 to 15. Examples of such carboxylic acids are:



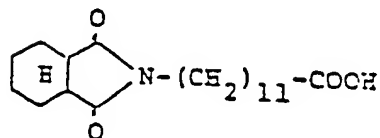
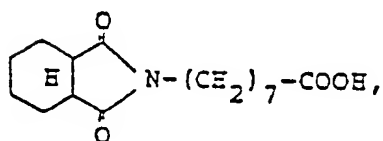
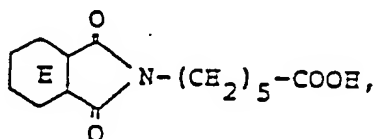
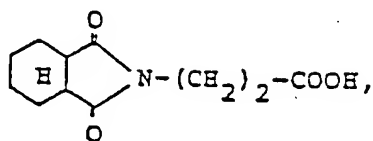
The following carboxylic acids also may be used:



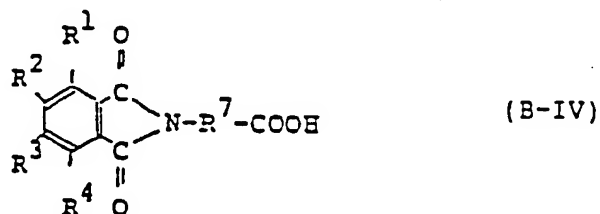
Among the carboxylic acids of the formula (B-I), the preferred carboxylic acids are those in which X represents an alicyclic group having the formula (B-II):

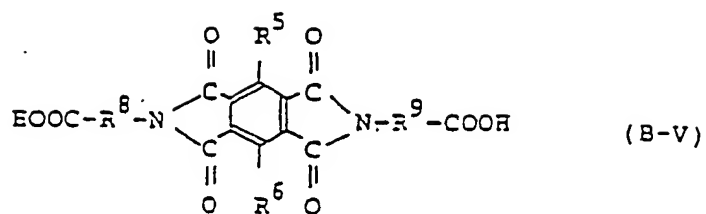


wherein n is an integer of 3 to 6, preferably, 4, and s is an integer of 1 to 15. Examples of such carboxylic acids are:

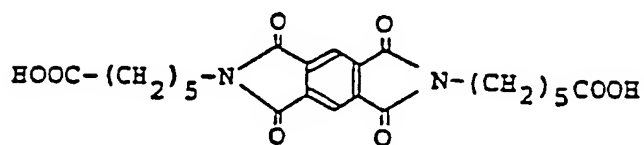
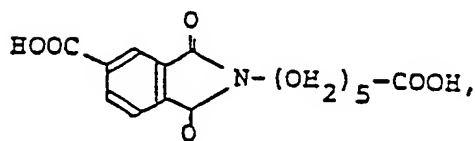
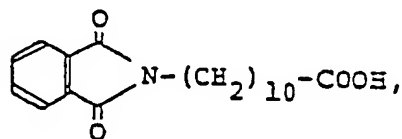
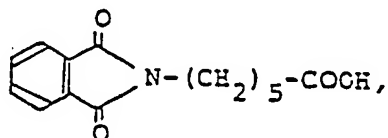
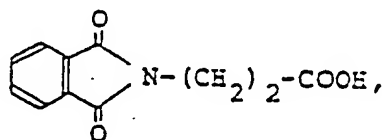


Among the carboxylic acids of the formula (B-I), the carboxylic acids in which X represents an aromatic group and which are preferably used in the composition of the present invention and phthalimide derivatives, trimellitimide derivatives and pyromellitimide derivatives which are represented by the formula (B-IV) or (B-V):

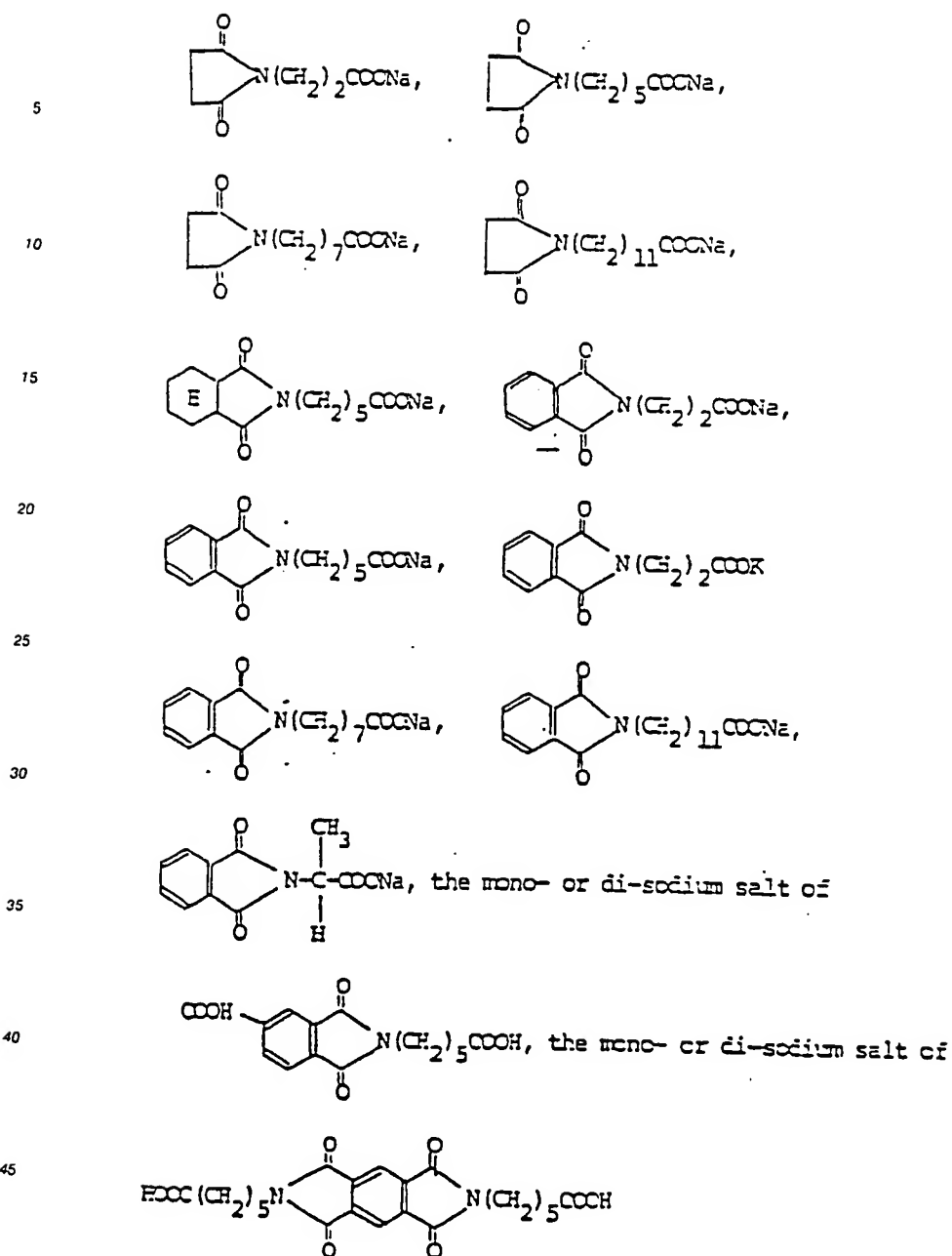




10 wherein,  $R^1$  to  $R^6$  represent, independently from each other, a group selected from the group consisting of a hydrogen atom, lower alkyl groups, aryl groups, aralkyl groups, halogen atoms, a carboxyl group, a nitro group, and an amino group; and  $R^7$  to  $R^9$  represent, independently from each other, a hydrocarbon group having not greater than 20 carbon atoms. Examples of such carboxylic acids are:



55 The alkali or alkaline earth metals constituting the salts of the above-mentioned carboxylic acids may include, for example, K, Na, Cs, Mg, Ca, Sr, and Ba. Of these, K and Na are preferable. Especially preferable examples are the following compounds:



Other examples of the crystallization promotor suitable as a component (B) are metal salts of organic polymers containing pendant carboxyl groups or carboxylic anhydride groups such as copolymers of olefins or aromatic olefins with unsaturated carboxylic acid or its anhydride. Examples of the olefin include ethylene, propylene and 1-butene, those of the aromatic olefins include styrene,  $\alpha$ -methylstyrene, vinyltoluene and isopropenyltoluene, those of the unsaturated carboxylic acid or its anhydride include acrylic acid, methacrylic acid crotonic acid, maleic acid, itaconic acid, maleic anhydride and itaconic anhydride. The copolymer may contain 50 to 99.8 mole %, preferably 60 to 99.5 mole %, more preferably 70 to 99 mole of the olefin unit or aromatic olefin unit.

The copolymer may be random copolymer, graft copolymer or block copolymer.

The number average molecular weight of the copolymer measured by gel permeation chromatography (GPC) at 40°C using tetrahydrofuran (THF) as a solvent, can be usually 1,000 to 50,000, preferably 2,000 to 30,000.

The molecular weight distribution (Mw/Mn) of the copolymer can be normally 1.1 to 20, preferably 1.2 to 15. Hereinabove, Mw means the weight average molecular weight and Mn means the number average molecular weight.

As the metal component of the metal salt of the organic polymer, alkaline metal such as sodium, potassium and cesium or alkaline earth metal such as magnesium, calcium and barium are exemplified. Among those metals, sodium and potassium are especially preferred.

The pendant carboxyl group or carboxylic anhydride group of the organic polymers is neutralized completely or partly. Neutralization degree of the carboxylic group or carboxylic anhydride group in the organic polymers, for example, can be 30 mole % to 100 mole %, preferably 30 mole % to 75 mole %. In determining the neutralization degree, it should be supposed that one carboxylic anhydride group corresponds to two carboxyl groups.

In those metal salts of the organic polymers, sodium salt of potassium salt of copolymer composed of ethylene and methacrylic acid are particularly preferred.

### Component (C)

The plasticizers (C) incorporated into the polyester composition of the present invention are those selected from the group consisting of the above-mentioned classes (C<sub>1</sub>), (C<sub>2</sub>), (C<sub>3</sub>) and (C<sub>4</sub>). These compounds may be used alone or in any mixture of two or more thereof.

In the compound of formula (I)

(HQ-R)<sub>2</sub>S,

R represents a hydrocarbon group selected from the group consisting of aliphatic hydrocarbon groups having at least two carbon atoms, alicyclic hydrocarbon groups, and aromatic hydrocarbon groups, and combinations thereof; two R groups may be the same as or different from each other. The aliphatic hydrocarbon groups include straight and branched aliphatic hydrocarbon groups usually having 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms. The alicyclic hydrocarbon groups are preferably those having not more than 10 carbon atoms, more preferably 4 to 6 carbon atoms and these hydrocarbon groups may have alkyl substituents on the ring. The aromatic hydrocarbon groups may have preferably 6 to 10 carbon atoms and may be benzene ring or at least one alkyl group-substituted benzene ring.

Q represents oxygen or sulfur. Two Q groups may be the same as or different from each other.

Examples of the compound of formula (I) are thiodiethanol, thiodipropanol, thiodibutanol, 2-hydroxypropyl sulfide, thiodicyclohexanol, thiodicyclopentanol, 2-methylmercaptoethyl sulfide, thiodibenzyl alcohol, and thiodiphenol.

The organic compounds condensed with a compound of the formula (I) to form the condensation product (C<sub>1</sub>) are those containing two alcoholic or phenolic hydroxyl groups. In this case, the compounds may contain two alcoholic or phenolic hydroxyl groups in one molecule, or they may contain alcoholic hydroxyl group and one phenolic hydroxyl group in one molecule.

These organic compounds may include, in addition to the compounds of the formula (I) themselves in which Q is oxygen, alkylene glycols described below in detail, divalent phenols such as hydroquinone, resorcinol, and bisphenol A; hydroxyalkylphenols such as p-methylolphenol, m-methylolphenol, and salicyl alcohol; and dihydroxycycloalkanes.

The condensation products (C<sub>1</sub>) may have molecular weight of from about 500 to 15,000, preferably from about 800 to 10,000.

The preferred condensation products (C<sub>1</sub>) are polythiodiethanol and a condensation product of thiodiethanol and an alkylene glycol. The polythiodiethanol is a compound of the formula [II]:

$\text{HO} \left( \text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{O} \right)_n \text{H}$  [II]

wherein n is preferably from 150 to 5, more preferably from 100 to 10.

The condensation product of thiodiethanol and an alkylene glycol will now be explained. The alkylene glycols may include, for example, ethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, diethylene glycol, and triethylene glycol. One of these alkylene glycols may be condensed with thiodiethanol. Alternatively, two or more of the alkylene glycols may be co-condensed with thiodiethanol. In this case, the thiodiethanol compound unit may be condensed in the form of a block or randomly. The latter case is more preferable. The condensation product usually contains at least 60 mole %, preferably at least 70 mole %, of the thiodiethanol component unit, and has preferably a molecular weight of 800 to 15,000.



To obtain the condensation products by reacting the compounds of formula (I) with phenols or alcohols, well known methods are used.

The ester compounds of the class (C<sub>2</sub>) will then be explained. The alcohol components usable for the preparation of the ester compound (C<sub>2</sub>) include, in addition to the compounds of the formula (I), the above-mentioned condensation products (C<sub>1</sub>), preferably polythiodiethanol, and condensation products of thiodiethanol and alkylene glycols. Even the condensation product (C<sub>1</sub>) having the smallest molecular weight may be used. The preferred upper limit of the molecular weight of the condensation product used is 15,000. Examples of the acids which, together with these alcohols, form the ester, are organic acids such as aliphatic organic acids, aromatic organic acids, and alicyclic organic acids. The aliphatic organic acids usable for the formation of the ester are those having preferably 2 to 20 carbon atoms, e.g., acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, stearic acid, and isomers thereof. The aromatic organic acids usable for the formation of the ester may have 7 to 20 carbon atoms and include, for example, benzoic acid, nitrobenzoic acid, toluic acid, phthalic acid, isophthalic acid, and terephthalic acid. Of these, benzoic acid is especially preferable. The alicyclic organic acids usable for the formation of the ester have 7 to 20 carbon atoms and may include, for example, cyclohexane carboxylic acid, cycloheptane carboxylic acid, and cyclohexane dicarboxylic acid.

The ester compounds (C<sub>2</sub>) may have a molecular weight of from 170 to 1,000 preferably from 250 to 800.

The especially preferred ester compounds (C<sub>2</sub>), are dibenzoate of thiodiethanol, dibenzoate of thiodipropanol, dibenzoate of a condensation product of thiodiethanol and diethylene glycol, and diacetate of thiodiphenol.

The ester compounds (C<sub>2</sub>) can be produced by well known methods.

The ether compound (C<sub>3</sub>) derived from a compound selected from the group consisting of the compounds of the formula (1) and the condensation products (C<sub>1</sub>), and a compound selected from the group consisting of monohydric alcohols and monohydric phenols will now be explained. The term "monohydric alcohol" as used herein refers to aliphatic alcohols alicyclic alcohols, and arylalkyl alcohols. Those alcohols may have 1 to 20 carbon atoms. The condensation product (C<sub>1</sub>) is preferably the same as that used for the ester compound (C<sub>2</sub>). Preferable examples of the condensation products (C<sub>3</sub>), are diphenyl ether of thiodiethanol, diphenyl ether of a condensation product of thiodiethanol and diethylene glycol, and dimethyl ether of thiodiphenol. Usually, condensation products (C<sub>3</sub>) may have a molecular weight of from 150 to 1,000, preferably from 250 to 800.

The modified polyolefin wax of the class (C<sub>4</sub>) is selected from oxydized polyolefin waxes, unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes, unsaturated epoxy compound-modified polyolefin waxes, unsaturated silane compound-modified polyolefin waxes and styrene type monomer-modified polyolefin waxes.

The polyolefin waxes usable as a raw material for the modified polyolefin waxes may include, for example, polyolefin waxes obtained by a method for the thermal decomposition or radical decomposition of polyolefins such as polyethylene, polypropylene, poly(4-methyl-1-pentene); polyethylene wax prepared by radical polymerization of ethylene under a high pressure; and polyolefin waxes obtained by polymerizing ethylene, propylene, or these olefins and  $\alpha$ -olefins such as, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-decene in the presence of transition metal compounds under a medium or low pressure. Of these polyolefin waxes, those comprising ethylene as the main component are preferable. For example, polyolefin waxes having at least 80 mole %, preferably at least 85 mole % of ethylene component, are most suitable. The polyolefin wax usually has an intrinsic viscosity  $[\eta]$  of 0.04 to 1.0 dl/g, preferably 0.06 to 0.8 dl/g, determined in decalin solution at a temperature of 135°C.

The oxidized polyolefin waxes usable in the present invention are those obtained by oxidizing the polyolefin waxes by means of any conventional method, for example, the methods described in United States Patent 3,892,717 and Japanese Unexamined Patent Publication No. 48-29876. The oxygen content of the oxidized polyolefin wax is usually in the range of from 0.1 to 11% by weight, preferably from 0.2 to 8% by weight. The oxygen contained in the wax is present in the form of a hydroxyl group, carbonyl group such as an aldehyde and a ketone, a carboxyl group, or the like. The oxidized polyolefin wax is also used as a raw wax for the production of the other modified polyolefin waxes as described hereinafter. The oxidized polyolefin wax may have an intrinsic viscosity  $[\eta]$  of 0.04 to 1.0 dl/g, preferably 0.04 to 0.7 dl/g, determined in decalin solution at a temperature of 135°C.

Those oxidized polyolefin waxes may be usable as raw materials from which the modified polyolefin waxes described hereinafter are derived.

Further, modified polyolefin waxes containing ester groups which are derived from the above oxidized polyolefin waxes and alcohols and/or organic acids, may also be usable as members of class (C<sub>4</sub>).

The unsaturated monomer useful for the preparation of the unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes include unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid, fumaric acid, tetra-hydrophthalic acid, itaconic acid, citraconic acid, crotonic acid, isocrotonic acid, Nadic Acid® (endo-cis-bicyclo[2.2.1]hepto-5-ene-2,3-dicarboxylic acid) and their derivatives such as acid  
 5 halides, amides, imides, anhydrides, and esters, e.g., malenyl chloride, maleimide, maleic anhydride, citraconic anhydride, monomethyl maleate, acrylic amide, dimethyl maleate, glycidyl maleate, methyl-(metha)acrylate, ethyl(metha)acrylate, n-butyl(metha)acrylate, and 2-ethylhexyl(metha)acrylate. Of these, anhydrides and esters of unsaturated carboxylic acids are preferable, and maleic anhydride, Nadic Anhydride®, ethyl(metha)acrylate, n-butyl(metha)acrylate, and 2-ethylhexyl(metha)acrylate are especially  
 10 preferable.

The graft-modified polyolefin waxes of the present invention can be prepared by an conventional method, e.g., by reacting monomers for polyolefin waxes in the presence of a radical initiator such as an organic peroxide, an organic perester and an azo compound under a condition in which the polyolefin waxes are melted.

15 The graft modification amount is usually from 0.2 to 50% by weight, preferably from 0.5 to 40% by weight, expressed in terms of the monomer content in the graft-modified polyolefin.

Those unsaturated carboxylic acids or derivative graft-modified polyolefin waxes may have an intrinsic viscosity of 0.04 to 1.0 dl/g, preferably 0.06 to 0.8.

The above-mentioned unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes also  
 20 may be used as a raw wax for the preparation of the other modified polyolefin waxes described hereinafter. Furthermore, modified polyolefin waxes containing ester groups which are derived from the unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes and alcohols also may be used as members of class (C<sub>4</sub>).

As the unsaturated epoxy compound-modified polyolefin waxes, those which are already known, e.g.,  
 25 those obtained by the method described in Japanese Unexamined Patent Publication No. 55-157613, can be directly used. The unsaturated epoxy compound can include allyl type unsaturated epoxy compounds, e.g., allyl glycidyl ether, 2-methylallyl glycidyl ether, and glycidyl ether of o-, m-, or p-allylphenol, 2-(o-, m-, or p-allylphenyl)ethylene oxide; styrene type unsaturated epoxy compounds such as glycidyl ether of isopropenyl phenol; and aliphatic unsaturated compounds containing epoxy groups, e.g., 3,4-epoxy-1-  
 30 butene, and 3,4-epoxy-3-methyl-1-butene. The unsaturated epoxy compound-modified polyolefin wax used preferably contains an epoxy group in an amount of  $10^{-4}$  to  $3 \times 10^{-2}$  gram equivalent per grams of the polyolefin wax.

Those unsaturated epoxy compound-modified polyolefin waxes may have an intrinsic viscosity of 0.04 to 1.0 dl/g, preferably 0.06 to 0.8.

35 The unsaturated silane compound-modified polyolefin waxes usable as the component (C) are those described in, for example, Japanese Unexamined Patent Publication No. 54-145785. That is, such polyolefin waxes are, for example, those graft-modified with vinyltrimethoxysilane, vinyltriethoxysilane, and vinyltris-(methoxyethoxy)silane. The graft percentage is usually from 3 to 45% by weight, preferably from 5 to 30% by weight.

40 The styrene type monomer-modified polyolefin waxes usable as the component (C) are those modified with styrene type monomer having 8 to 11 of carbon atoms, e.g., styrene,  $\alpha$ -methylstyrene, p-methylstyrene, o-methylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, and the like, according to the method described for the above-mentioned modified polyolefin waxes modified with unsaturated carboxylic acids, or the like. More specifically, styrene type monomer-modified polyolefin waxes prepared by the method  
 45 described in, for example, Japanese Unexamined Patent Publication No. 58-65713. The content of the styrene type monomer in the modified waxes is usually from 1 to 90% by weight, preferably from 5 to 75% by weight. As described hereinabove, modified waxes obtained by graft modifying the oxidized polyolefin waxes and the unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes with styrene type monomer are also included in the styrene type monomer-modified polyolefin waxes used in the present  
 50 invention.

Those styrene type monomer-modified polyolefin waxes may have an intrinsic viscosity of 0.04 to 1.0 dl/g, preferably 0.06 to 0.8 dl/g.

Of the above-mentioned modified polyolefin waxes (C<sub>4</sub>), oxidized polyolefin waxes, oxidized polyolefin waxes further grafted with styrene type monomers, and  $\alpha,\beta$ -unsaturated carboxylic acid ester-grafted  
 55 polyolefin waxes are especially preferable.

The compounding ratio of component (B) to polyester (A) is in the range of from 0.05 to 15 parts by weight, preferably from 0.1 to 10 parts by weight, more preferably 0.2 to 10 parts by weight per 100 parts by weight of the polyester (A). Similarly, the compounding ratio of component (C) to polyester (A) is in the range of from 0.1 to 15 parts by weight, preferably 0.2 to 10 parts by weight, more preferably 0.5 to 10 parts by weight, most preferably 1 to 10 parts by weight per 100 parts by weight of the polyester (A).

As long as the compounding ratios of components (B) and (C) to polyester (A) are in the above-specified ranges, improved effects of satisfactory rate of crystallization and satisfactory heat resistance which are characteristic of the composition of the present invention are realized.

Although the polyester composition of the present invention may consist only of the above-mentioned essential three components, polyester (A), and components (B) and (C), it may contain various compounding agents or additives conventionally used for polyesters as long as the utility of the composition is not impaired. Examples of such compounding agents or additives are reinforcing fillers such as diatomaceous earth, calcium carbonate, silica, silica-alumina, alumina, carbon, mica, titanium oxide, carbon fiber, glass fiber, and aramide fiber; lubricants; surfactants; thickening agents such as pentaerythritol, trimellitic acid and pyromellitic acid; flame-retardants; ultraviolet light stabilizers; antioxidants; releasing agents; and coloring agents. The compounding proportion of these compounding agents or additives may be appropriately selected.

Furthermore, the polyester composition of the present invention may contain at least one polymer selected from the group consisting of, for example, polyolefins, olefin copolymers or modified polymers thereof, polystyrene, polyamides, polycarbonates, polyacetals, polysulfone, polyphenylene oxides, fluoroplastics, silicone resin, and epoxy resins.

The polyester composition of the present invention can be obtained by a method wherein a polymer mixture consisting of the essential components and, if necessary, the compounding agents or additives is melt mixed by any conventional method.

The present invention will now be explained in detail by the following examples.

In the examples, the molding and evaluation of the polyester composition were carried out by the following methods.

#### 30 Press molding

A dried polyester composition was pressed at a molding temperature of 290°C; by using a pressing machine to prepare a quenched pressed sheet having a size of 15 cm x 10 cm x 0.2 cm.

#### 35 Injection molding

A specimen for bending test having a thickness of 0.2 cm was prepared at a mold temperature of 70°C; by using an injection molding machine Model IS-35P manufactured by Toshiba Kikai Kabushiki Kaisha.

#### 40 Bending test

A strip specimen 1.27 cm wide by 6.35 cm long cut from the pressed sheet or an injection molded specimen of the same size was subjected to a bending test at a temperature of 23°C and at a crosshead speed of 5 mm/min. by using a tensile testing machine model 1122 manufactured by Instron Company.

#### 50 Heat resistance

A strip specimen 1.27 cm wide by 2 cm long cut from the pressed sheet or injection molded specimen was determined for temperature dependence of elastic modulus by using a Dynamic Mechanical Analyzer Model 981 manufactured by DuPont Company. The ratio of the elastic modulus at 100°C ( $E_{100}$ ) to the elastic modulus at 30°C ( $E_{30}$ ), i.e.,  $E_{100}/E_{30}$ , was used as an indication of the heat resistance.

$T_{ch}$ ,  $\Delta H_H/\Delta H_C$

These values were determined by using a differential analyzer (abbreviated as DSC, Type II manufactured by Perkin Elmer Company). That is, about 5 mg of a sample was weighed out from the quenched pressed sheet or the injection molded sheet. Then the sample was subjected to DSC measurement under condition in which the sample is heated at an increasing rate of 20°C/min. from room temperature, is held at a temperature of 290°C for 5 min., and is thereafter cooled at an decreasing rate of 20°C/min. The crystallization temperature  $T_{CH}$  during the increase in temperature, the quantity of heat  $\Delta H_H$  determined a peak area appearing at  $T_{CH}$ , and the quantity of heat  $\Delta H_C$  determined from a peak area appearing at the crystallization temperature during the decrease in temperature were measured from the resultant curve of heat. The thus-obtained  $T_{CH}$  is an indication of the low temperature mobility of the polyester molecule. The  $\Delta H_H/\Delta H_C$  is an indication of the crystallizability of the polyester. The smaller the values of  $T_{CH}$  and  $\Delta H_H/\Delta H_C$ , the more crystallizable the polyester.

#### Examples 1 to 12, Comparative Examples 1 to 5 and Reference Example 1

A polyethylene terephthalate having an intrinsic viscosity of 0.65 dl/g, a plasticizer such as a thiodiethanol derivative and various crystallization promoters were dry blended in the proportion indicated in Table 1. The resultant mixtures were melt mixed by using a 20 mm  $\phi$  extruder (a Dilmage type screw and, in the case where glass fiber is blended, a full-flighted screw, L/D = 28). The physical properties of the polyester compositions thus obtained were evaluated. The results are shown in Table 1.

In Table 1, the symbols represent the following:

(1) C-1 in plasticizer component (C) is a polyethylene glycol (manufactured by Nippon Oils & Fats Co., Ltd., Polyethylene glycol 4000).

(2) C-2 in plasticizer component (C) is dibenzoate in thiodiethanol.

(3) C-3 in plasticizer component (C) is a copolymer ether of thiodiethanol and diethylene glycol. This compound was synthesized in the following manner.

A reaction vessel was charged with 200 g of thiodiethanol, 50 g of diethylene glycol, and 0.625 g of phosphorus acid. The mixture was reacted under a nitrogen atmosphere at a temperature of 195°C for 8 hours while the formed water was distilled off, after which the reaction was continued under a reduced pressure of 500 mmHg for a further period of 5 hours. The resultant product was a pale yellow liquid polymer. This polymer had a number average molecular weight of 3,600, determined in GPC (THF solvent, 40°C).

(4) C-4 in plasticizer component (C) is dibenzoate of thiodipropanol.

(5) C-5 in plasticizer component (C) is diacetate of thiodiphenol.

(6) C-6 in plasticizer component (C) is dimethyl ether of thiodiphenol.

(7) C-7 in plasticizer component (C) is dibenzoate of 2-mercaptoethyl sulfide.

(8) B-1 in crystallization promoter (B) is talc.

(9) B-2 in crystallization promoter (B) is the sodium salt of an ethylene/methacrylic acid copolymer (manufactured by DuPont Company, Surlyn® 1605 ethylene content of 95 mole %, Melt Flow Index of 2.8, measured at temperature of 190°C, under load of 2.16kg).

(10) B-3 in crystallization promoter (B) is the sodium salt of a styrene/methacrylic acid copolymer. This compound was synthesized in the following manner.

A reaction vessel provided with a stirrer was charged with 624 g of styrene, 33.8 g of methacrylic acid and 920 ml of toluene. After nitrogen bubbling for 15 minutes, the reaction vessel was sealed with nitrogen and the contents of the reaction vessel were heated to a temperature of 100°C. A dropping funnel was charged with 2 g of benzoyl peroxide and 60 ml of toluene. After nitrogen bubbling for 15 minutes, the mixture in the funnel was dropped into the reaction vessel over a period of about 30 minutes. After completion of the dropping, the reaction was continued for 4 hours. The reaction mixture was then poured into a large excessive amount of hexane to allow the reaction product to precipitate. The yield of the resultant polymer was 292 g. The polymer had a number average molecular weight  $M_n$  of 84,000, determined in GPC (THF solvent, 40°C), and a molecular weight distribution  $M_w/M_n$  of 1.5. The content of methacrylic acid in the polymer was determined by elemental analysis and was found to be 10 mole %.

A reaction vessel provided with a condenser was charged with 200 g of the styrene/methacrylic acid copolymer synthesized according to the above-mentioned method and 1200 ml of toluene. The contents of the reaction vessel were heated to a temperature of 100°C. An aqueous solution containing 6.18 g of NaOH was dropped into the reaction vessel through a dropping funnel over 5 minutes. The reaction was continued for a further 4 hours. The reaction mixture was poured into hexane to allow the reaction product to precipitate. The precipitated polymer was recovered. The resultant polymer exhibited a degree of neutralization of 75%.

(11) B-4 is a crystallization promotor (B) is sodium benzoate (manufactured by Wako Pure Chemical Industries, Ltd. in Japan).

#### Examples 13 to 32 and Comparative Examples 6 to 9

A polyethylene terephthalate having an intrinsic viscosity of 0.65 dl/g, a crystallization promotor, and a modified polyolefin wax as a plasticizer were dry blended in the proportions indicated in Table 1. The resultant mixtures were melt mixed by using a 20 mmφ extruder (a Dulmage type screw and, where glass fiber is blended, a full-flighted screw, L/D = 28). The physical properties of the thus-obtained polyester compositions were evaluated. The results are shown in Table 2. It is apparent from Table 2 that the compositions of the present invention are superior in various properties to the corresponding compositions comprising only the components (A) and (B).

In Table 2, the symbols represent the following:

- (1) B-6 is sodium stearate.
- (2) B-7 is sodium 5-(N-phthalimide)-caproate.
- (3) B-8 is the sodium salt of a styrene/methacrylic acid copolymer (content of methacrylic acid: 15 mole %, degree of neutralization: 75%). This compound was synthesized in the same manner as that described for the synthesis of B-3.
- (4) C-8 is a sample comprising a polyethylene wax having a  $[\eta]$  of 0.23 dl/g with which 14 wt. % of n-butyl methacrylate was graft polymerized. This sample was synthesized according to the following method and various modified waxes were synthesized according to the same method.

#### Preparation Example of Graft-Modified Polyolefin Wax

595 g of a polyethylene wax having a  $[\eta]$  of 0.23 dl/g was charged into a glass reaction vessel having a capacity of 1 l, and was melted at a temperature of 140°C. Then, 105 g of n-butyl methacrylate and 9.0 g of di-tert-butyl peroxide were added to the reaction vessel. The mixture was reacted with heat for 4 hours. Then the reaction mixture was degassed under a vacuum pressure of 10 mmHg while it was maintained at a temperature of 140°C, so as to remove the volatile matters. Thereafter, the reaction product was cooled and solidified. The resultant n-butyl methacrylate grafted polyethylene wax has a n-butyl methacrylate graft percentage of 14% by weight.

(5) C-9 is a modified polyethylene wax with 40% by weight of n-butyl methacrylate graft-copolymerized therewith (a wax having a  $[\eta]$  of 0.07 dl/g and containing 2 mole % of propylene copolymerized therewith was used as the starting material to be modified).

(6) C-10 is a polyethylene wax with 30% by weight of ethyl methacrylate copolymerized therewith (a polyethylene wax having a  $[\eta]$  of 0.13 dl/g and a propylene content of 4 mole % was used as the starting material).

(7) C-11 is a polyethylene wax with 50% by weight of 2-ethylhexyl methacrylate graft-copolymerized therewith (the starting material was the same as that for C-9). Quantity of heat  $\Delta H_w/\Delta H_c$  is an indication of the crystallizability of the polyester. The smaller the values of  $T_{CH}$  and  $\Delta H_w/\Delta H_c$ , the more crystallizable the polyester.

(8) C-12 is a polyethylene wax with 10% by weight of 2-ethylhexyl methacrylate graft-copolymerized therewith (the starting material was the same as that for C-8).

(9) C-13 is an oxidized wax having an oxygen content of 4.9% by weight (a polyethylene wax having a  $[\eta]$  of 0.23 dl/g and a propylene content of 4 mole % was used as the starting material).

(10) C-14 is an oxidized wax having an oxygen content of 7.0% by weight (the starting material was the same as that for C-8).

(11) C-15 is a modified wax comprising an oxidized wax having an oxygen content of 0.9% by weight with which 35% by weight of styrene was graft-copolymerized (the starting material was the same as that for C-9).

(12) C-16 is a wax to which 20% by weight of styrene and 10% by weight of acrylonitrile were co-grafted (the starting material was the same as that for C-10).

(13) C-17 is a maleic anhydride-grafted wax having a potassium hydroxide number of 30 mg g (the starting material was the same as that for C 10).

(14) C-18 is a wax with 7% by weight of vinyl-methoxysilane grafted thereto (the starting material was the same as that for C-8).

(15) C-19 is a wax containing allyl glycidyl ether grafted thereto and having an epoxy group content of  $9 \times 10^{-4}$  gram equivalent per g of the wax (the starting material was the same as that for C-8).

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TABLE 1. PHYSICAL PROPERTIES<sup>a)</sup> OF POLYESTER COMPOSITION

Comparative Examples	Crystallization Promoter Component <sup>b)</sup> (B)		Plasticizer Component (C)		E <sub>100/30</sub>	Bending Strength <sup>b)</sup> (kg/cm <sup>2</sup> )	Bending Modulus (kg/cm <sup>2</sup> )	T <sub>GI</sub> (°C)	ΔH <sub>H</sub> /ΔH <sub>C</sub>
	Type	Compounding Amount (part by weight) <sup>b)</sup>	Type	Compounding Amount (part by weight) <sup>b)</sup>					
1	None	-	None	-	0.003	920	31000	146	0.575
2	B-1	1	None	-	0.014	880	28000	130	0.416
3	B-2	5	None	-	0.065	890	27400	125	0.327
4	B-3	5	None	-	0.087	1050	35000	124	0.384
5	None	-	C-2	5	0.001	970	33100	124	0.391
Reference Example 1	B-3	5	C-1	5	0.114	1040	35200	121	0.227
2	B-3	5	C-2	3	0.147	1090	37800	111	0.082
3	B-3	5	C-2	5	0.168	1140	41200	110	0.065
4	B-1	1	C-2	3	0.084	980	32400	117	0.212
5	B-2	5	C-2	3	0.132	990	33000	112	0.100
6	B-2	5	C-3	5	0.129	1010	32800	114	0.160
7	B-3	5	C-3	3	0.230	1000	38100	112	0.113
8	B-4	0.2	C-2	3	0.117	1020	37000	112	0.099
9	B-2	5	C-4	5	0.098	980	31000	119	0.213
10	B-2	5	C-5	3	0.096	970	31200	118	0.208
11	B-3	5	C-6	5	0.101	1020	35800	116	0.212
12	B-2	5	C-7	3	0.078	960	31000	119	0.311
	B-3	5	C-2	3	0.392	2270	118700	108	0.310

a) In Example 12, the physical properties of an injection molded article containing 30% by weight of glass fiber were shown. In the other Examples and Comparative Examples, the physical properties of pressed sheets were shown.

b) A value based on 100 parts by weight of polyethylene terephthalate.

TABLE 2. PHYSICAL PROPERTIES<sup>a)</sup> POLYESTER COMPOSITION

	COMPONENT (B)		COMPONENT (C)		E <sub>100/30</sub>	Bending Strength (kg/cm <sup>2</sup> )	Bending Strength (kg/cm <sup>2</sup> )	$\Delta H/\Delta H_C$
	Type	Compounding Amount (part by weight) <sup>b)</sup>	Type	Compounding Amount (part by weight) <sup>b)</sup>				
Comparative Example	6	0.2	None	-	0.013	900	29800	0.462
	7	0.2	None	-	0.037	1010	31600	0.390
	8	3	None	-	0.101	1020	34600	0.213
	9	-	C-8	5	0.002	840	27200	0.455
Example	13	0.2	C-8	5	0.044	950	30500	0.246
	14	0.2	C-8	5	0.066	1010	32800	0.233
	15	5	C-8	5	0.123	950	31000	0.200
	16	5	C-8	5	0.169	1070	36000	0.080
	17	5	C-8	2	0.157	1040	35800	0.106
	18	3	C-8	5	0.213	1020	37000	0.087
	19	5	C-9	3	0.133	990	34900	0.100
	20	4	C-10	5	0.141	1010	33800	0.105
	21	3	C-11	5	0.185	960	32400	0.097
	22	3	C-12	5	0.166	1030	34300	-

Table 2 is continued on the next page ....



TABLE 2. PHYSICAL PROPERTIES<sup>a)</sup> POLYESTER COMPOSITION (continued)

COMPONENT (B)		COMPONENT (C)		E <sub>100/30</sub>	Bending Strength (kg/cm <sup>2</sup> )	Bending Modulus (kg/cm <sup>2</sup> )	$\Delta\eta_B/\Delta H_C$
Type	Compounding Amount (part by weight) <sup>b)</sup>	Type	Compounding Amount (part by weight) <sup>b)</sup>				
Example 23	5	C-13	5	0.190	1020	33700	0.200
24	5	C-14	5	0.199	1000	35000	0.141
25	3	C-15	4	0.135	1020	34600	0.128
26	3	C-16	3	0.122	980	30300	0.194
27	5	C-17	5	0.098	990	30700	0.225
28	5	C-18	4	0.084	930	30400	0.210
29	5	C-19	4	0.096	960	31200	0.186
30	3	C-15	3	0.392	1900	10800	0.032
31	5	C-8	3	0.411	2030	10700	0.029
32	0.3	C-2	3	0.082	1090	36500	0.297

a) In Examples 30 and 31, the physical properties of injection molded articles containing 30% by weight of glass fiber are shown. In the other Examples and Comparative Examples, the physical properties of pressed sheets are shown.

b) A value based on 100 parts by weight of polyethylene terephthalate.

## Claims

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1. A polyester composition comprising:

(A) 100 parts by weight of substantially linear polyester comprising, as the main constituent unit, ethylene terephthalate;

(B) 0.05 to 15 parts by weight of crystallization promotor; and

10 (C) 0.1 to 15 parts by weight of at least one modified polyolefin wax plasticizer selected from oxidized polyolefin waxes, unsaturated carboxylic acid or its derivative graft-modified polyolefin waxes, unsaturated epoxy compound-modified polyolefin waxes, unsaturated silane compound-modified polyolefin waxes, and styrene-type monomer-modified olefin waxes.

2. A composition according to any preceding claim wherein the modified polyolefin wax C is derived from polyolefin wax having an intrinsic viscosity  $[\eta]$  of 0.04 to 1.0 dl/g, determined in decalin solution at a temperature of 135°C.

3. A composition according to any preceding claim wherein the modified polyolefin wax C is derived from polyolefin wax comprising ethylene as the main component.

4. A composition according to any preceding claim wherein the modified polyolefin wax C is selected from oxidized polyolefin wax, oxidized polyolefin wax further grafted onto styrene type monomer and  $\alpha, \beta$ -unsaturated carboxylic acid ester-grafted polyolefin wax.

5. A composition according to any preceding claim wherein the polyester contains at least 70 mole % of ethylene terephthalate units.

6. A composition according to any preceding claim wherein the crystallization promotor (B) is selected from sodium and potassium salts of organic carboxylic acids; alkali metal and alkaline earth metal salts of organic acids containing an imide linkage and having not more than 50 carbon atoms; and metal (e.g. sodium, potassium) salts of copolymer of olefin or aromatic olefin with unsaturated carboxylic acid or anhydride.

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